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(54) Title: AQUEOUS PESTICIDAL MICROEMULSION COMPOSITIONS (57) Abstract The present invention generally relates to an aqueous-based pesticidal microemulsion formulation which comprises a pesticidally active compound, a surfactant mixture and water, wherein said surfactant mixture comprises an ethoxylated acid, an alkyl polyc side, an thoxylated castor oil, optionally, an ethoxylated alkyl phenyl phosphate and a cosurfactant; the remainder being water. The invention also relates to methods of preparing said microemulsions.		

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AQUEOUS PESTICIDAL MICROEMULSION COMPOSITIONS

Field of The Invention

5 The present invention relates to aqueous based pesticidal microemulsion and to methods for preparing same.

Background of the Invention

10 In recent years, the plant protection industry has been coming under more pressure from environmental groups and governmental legislation to improve herbicidal/pesticidal formulations. One of the greatest pressures is to reduce the quantity of aromatic petroleum based solvents from all formulations, which has had a significant effect on the acceptability of emulsifiable concentrate (EC) formulations.

15 Another growing tendency in the industry is towards formulations containing less active ingredients. This not only reduces costs, but also addresses the concerns of environmentalists and end users. This has led to an increased importance for adjuvants used to promote the efficacy of herbicide/pesticides.

20 Microemulsions are a unique class of thermodynamically stable mixtures of water, oil (pesticidal actives) and surface active agents in one phase which are an attractive alternative to EC's because of their increased stability, lack of organic solvent and ease of use. Microemulsions form spontaneously and are indefinitely storage stable. As a rule, however,
25 microemulsions are difficult to formulate and are obtainable only with certain surfactant combinations and only within specific finite concentrations of these surfactant combinations.

U.S. Statutory Invention Registration H303 describes a composition of matter and a method of treating agricultural substrat s in which an active ingredient, which may be a herbi-
 5 cide, is utilized in conjunction with an amount of a glycoside dispersing agent selected from the group consisting of fructo-
 side, glucoside, mannoside, galactoside, taloside, guloside, alloside, altroside, idoside, arabinside, xyloside, lyxoside an
 riboside and mixtures thereof in an amount sufficient to form :
 emulsion or dispersion of the active ingredient.

10 U.S. Patent No. 5,227,402 describes plant protection agent based on aqueous microemulsions which contain, as emulsifiers, ethoxylated and phosphorylated, styryl-substituted phenols or
 salts thereof in combination with one or more non-phosphorylate
 15 emulsifiers belonging to the group comprising salts of (C₁₀-C₁₆) alkyl-monoglycol to -hexaglycol ether-sulfates, salts of α-(C₁₄-
 C₁₉)-alkenol sulfates, salts of optionally chlorinated (C₁₃ - C₁₈ alkanesulfonic acids, salts of dodecylphenylsulfonic acid, amir
 oxethylates or α(C₉-C₂₀)-alkyl-ω-hydroxypolyoxylethylenes contain
 ing 2 to 22 moles of ethylene oxide.

20 EP 0 371 212 describes aqueous herbicidal microemulsions containing 1,2-dimethyl-3,5 diphenylpyrazolium (difenzoquat), a
 essentially water insoluble active ingredient and a nonionic
 surfactant.

GB 2,089,914 is directed to aqueous phenoxy emulsions whic
 25 comprise 30-75% by weight of one or more herbicidally-active phenoxyalkanecarboxylic acid esters, 1.01 to 11.1 parts by weig
 per 100 parts of ester of oil-soluble emulsifiers which are soluble in the esters and have an HLB value of 9 to 16, and one
 or more ionic or nonionic water-soluble dispersants.

30 GB 2,115,285 describes emulsions similar to those describe in GB 2,089,914 with the exception that the emulsion of GB

2,115,285 additionally comprises 0.1 to 3 parts by weight of one or more alkali metal salts of single or multiple unsaturated fatty acid taurides or fatty acid alkyl taurides as water soluble dispersants.

5 The object of the present invention is to provide microemulsion formulations which are comparable to emulsifiable concentrate systems but which do not contain undesirable aromatic, hydrocarbon solvents.

10 A further object is to provide aqueous based microemulsions which are environmentally acceptable and uniquely stable.

15 Another object of the present invention is to provide a surfactant package which allows one to prepare highly concentrated, stable, aqueous microemulsions and promotes the efficacy of the herbicidal actives in said microemulsions which leads to reduced application rates.

Summary of the Invention

20 The present invention generally relates to an aqueous based pesticidal microemulsion formulation which comprises a pesticidally active compound, a surfactant mixture and water, wherein said surfactant mixture comprises an ethoxylated acid, an alkyl polycoside, an ethoxylated castor oil, optionally, an ethoxylated alkyl phenyl phosphate and a cosurfactant; the remainder being water.

25 The present invention also relates to methods of preparing said microemulsions.

Detailed Description of the Invention

The present invention relates to aqueous-based pesticidal microemulsions which comprise at least one pesticidally active compound, a surfactant mixture and water, wherein said
5 surfactant mixture comprises at least one ethoxylated acid, at least one alkyl polycoside, at least one ethoxylated castor oil optionally at least one ethoxylated alkyl phenyl phosphate and least one cosurfactant.

The present invention also relates to a surfactant mixture
10 useful in formulating said microemulsions, wherein said surfactant mixture comprises at least one ethoxylated acid, at least one alkyl polycoside, at least one ethoxylated castor oil optionally at least one ethoxylated alkyl phenyl phosphate and least one cosurfactant.

15 The concentrated microemulsion of the present invention generally comprises from about 1 to 98% by weight actives, from about 3 to 40% surfactant mixture, and water to 100%. The present microemulsion preferably comprises from about 20 to 95% by weight actives, from 5 to 35% by weight surfactant mixture,
20 and water to 100%. In an especially preferred embodiment, the microemulsion of the present invention comprises from about 35% to about 85% by weight actives, from 10 to 30% by weight surfactant mixture, and water to 100%.

In usage, the concentrated microemulsion of the present
25 invention is diluted with water to the desired dilution level application rate. Typically, the concentrated microemulsion of the present invention is diluted with water to yield an aqueous based microemulsion containing from about 0.05 to about 50% by weight pesticidal active, more preferably from about 1 to 35% by
30 weight actives, and still more preferably from about 1.5 to 30% actives. The diluted microemulsions range in opacity from clear

to milky depending on the weight % of the actives in the concentrate.

Actives which can be employed in the microemulsion of the present invention include but are not limited to insecticides, nematocides, herbicides, fungicides, plant growth regulators and combinations thereof.

Pesticidal actives which can be employed in the context of the present invention include phenoxy-type (e.g., 2,4-D), dinitro-type (e.g. trifluralin), amide-type (e.g. propanil), organo phosphate-type (e.g., azinophos-methyl), urea-type (e.g., diuron), triazine type (e.g., atrazine), uracil-type (e.g., bromacil), sulfonyl urea-type (e.g., nicosulfuron), benzoic-type (e.g., dicamba), diaryl ether-type (e.g., fluazifop-butyl) and nitrile-type (e.g., bromoxynil) pesticides, along with triazole-based fungicides such as azaconazole.

Examples of pesticidal actives which are preferred include but are not limited to esters of 4-chloro-2-methylphenoxy-acetic (MCPA) acid bromoxynil esters and esters of 2,4-dichlorophenoxy acetic acid (2,4-D), as well as acetochlor, bupirimate, butylate, chlorbufam, flurochloridone, esters of 2,4-DB acid, any dichlorprop ester, any fenoprop ester, fenpropimorph, fluoroglycofen-ethyl, fluroxpyr, ioxynil esters, esters of MCPB, mecoprop esters, metolachlor, molinate, propiconazole, pyridate, sethoxydim, 2,4,5-T ester, tebutam, triclopyr, azaconazole, triadimefon, thidiazuron, prometryn, bentazon, lactofen, acifluorin sodium, fomesufen, quizazifop-ethyl, diclofop-methyl, fluazifop-butyl, imazaquin, imazethapyr, thifensulfuron-methyl, chlorimuron, chlorimuron-ethyl and primisulfuron and vernolat.

Especially preferred active ingredients are essentially water insoluble and include: straight or branched C_4 - C_{10} alkyl esters of 2,4-D acid and mixtures thereof; straight or branched

C₄-C₁₀ alkyl esters of MCPA acid and mixtures thereof; and/or bromoxynil esters of straight or branched C₄-C₁₀ alkanolic acids and mixtures thereof. The isooctyl ester of 2,4-D acid, C₈H₁₇ esters (mixed butyl esters) of MCPA acid and bromoxynil octano or mixtures thereof are especially preferred. In some circumstances, desirable results can be obtained by utilizing combination of both the ester form of the pesticidal active and its parent acid.

Aqueous formulations of these pesticidally active ingredients are normally prepared using the salts of these compounds which are water soluble, and not the esters. However, it has been found in some instances that an ester can be more effective because many of these essentially water insoluble pesticidally active ingredients are normally applied post-emergence to the foliage of the undesirable plant and the leaf penetration properties of the pesticide can be advantageously altered using various lipophilic esters and/or acids of these pesticides.

The ethoxylated acid of the surfactant mixture of the present invention preferably contains from about 2 to 22 moles ethylene oxide. An ethoxylated oleic acid having from 2 to 22 moles of ethylene oxide is a preferred example. Examples of preferred ethoxylated acids include Ethofat®0/15 and Ethofat®242/25 both of which are sold by Akzo Nobel Chemicals, Inc. The surfactant mixture of the microemulsion of the present invention generally comprises from about 0.5 to 40% by weight ethoxylated acid. Still more preferred, said microemulsion contains from 1 to 30% and still more preferred 1.5 to 25% by weight ethoxylated acid.

Alkyl polycosides useful in the surfactant mixture of the present invention include those prepared in accordance with U.S. Patent Numbers 3,219,656 and 3,598,865, which are incorporated

herein by reference. The alkyl polycosides of the present invention generally comply with the following general formula:



wherein R contains from 1 to about 30 carbon atoms, G is the saccharide backbone (glycosyl) of the molecule and x, which refers to the degree of saturation, is from 1 to 18. Useful saccharide moieties for the glycoside include, but are not limited to fructosides, mannosides, glucosides, talosides, galactosides, gulosides, allosides, altrosides, idosides, anabinosides, lyxoside, xylosides, ribosides and mixtures thereof. Preferred saccharide moieties include glucosides, xylosides and fructosides. Glycoside®APG 325 (C₉-C₁₁) which can be purchased from Henkel Corporation is an alkyl polycoside which is preferably employed in the surfactant mixture of the present microemulsion. Also suitable for use in the present invention is Berol AE6202 which is an alkyl polyglycoside which can be purchased from Akzo Nobel Chemicals, Inc.

The surfactant mixture of the present invention generally contains from about 0.1 to about 20% by weight alkyl polycoside. Still more preferred, from about 1.0 to 15% by weight alkyl polycoside is employed.

The surfactant mixture also comprises from about 0.1 to about 45% by weight of ethoxylated castor oil, and still more preferred, from about 2 to 25% by weight. Preferred ethoxylated castor oils have from between about 5 to 55 moles of ethylene oxide chemically combined with each mole of castor oil. Particularly good results are obtained with Alkamuls® EL 620 (30 EO) which is manufactured by Rhone Poulenc, and Berol 106 which is available from Akzo Nobel Chemicals, Inc.

Suitable ethoxylated alkyl phenyl phosphates are styryl-containing ethoxylated and phosphorylated phenols and more preferred, phenols of this type having three styrene radicals and

approximately 16 to 20 moles of ethylene oxide. Soprophore 3D (thoxylate tristysol phenyl phosphate) which is manufactured by Rhone Poulenc is a preferred thoxylated alkyl phenol phosphate. Generally, the surfactant package of the present invention comprises from about 0 to about 25% by weight of ethoxylated alkyl phenol phosphate is incorporated into the surfactant mixture of the present invention. A more preferred range of alkyl phenyl phosphate is between about 2 to about 15 wt%.

The surfactant mixture of the present invention comprises from about .1 to 45% by weight, and more preferably, from about 10 to about 25% cosurfactant. Preferred cosurfactants are usually medium chain fatty alcohols, acids or amines. The cosurfactant is preferably an alcohol of the formula R-OH wherein R is a straight or branched chain alkyl with 4 to 10 carbon atoms. Especially preferred cosurfactants are alcohols of the above formula wherein the R group is a straight chain alcohol containing from 5 to 8 carbon atoms. Examples of preferred alcohols are pentanol, hexanol, heptanol, octanol and mixtures thereof, with hexanol being the most preferred.

In one embodiment, the present invention relates to an aqueous herbicidal microemulsion which comprises at least one herbicidally active component, a surfactant mixture and water, wherein comprises said surfactant mixture comprising of 0.5 to 40% by weight of an ethoxylated acid, 0.1 to 20% by weight of an alkyl polycoside, 0.1 to 45% by weight of an ethoxylated castor oil, 0 to 25% by weight of an ethoxylated alkyl phenyl phosphate and a cosurfactant; and water to 100%.

In another embodiment, the aqueous-based herbicidal microemulsion of the present invention comprises from 1 to 98% herbicidal actives; from 3 to 40% surfactant mixture and the remainder water; wherein said herbicidally active material is selected from 2,4-D isooctyl ester, MCPA, trifluralin, propanil

and mixtures thereof; and said surfactant mixture comprises of 0.5 to 40% by weight ethoxylated oleic acid; 0.5 to 20% by weight alkyl polycoside; .5 to 35% by weight of an ethoxylated castor oil; 0 to 15% by weight of an ethoxylated alkyl phenyl phosphat ,
5 and an alcohol as a cosurfactant; the remainder being water.

In still another embodiment, the aqueous-based herbicidal microemulsion of the present invention comprises from 35 to 98% herbicidal actives; from 3 to 40% surfactant mixture and the remainder water; wherein said herbicidally active material is
10 selected from 2,4-D iso octyl ester, MCPA and mixtures thereof; and said surfactant mixture comprises of 1 to 30% by weight ethoxylated oleic acid; 1 to 25% by weight alkyl polycoside; 2 to 25% by weight of ethoxylated castor oil; 2 to 15% by weight of an ethoxylated alkyl phenyl phosphate, and 0.1 to 40% by weight
15 hexanol as a cosurfactant; the remainder being water.

In a most preferred embodiment, the microemulsion of the present invention comprises from 50 to 98% herbicidal actives; from 3 to 40% surfactant mixture, and the remainder water; wherein said herbicidally active material is selected from 2,4-D
20 iso octyl ester, MCPA and mixtures thereof; and said surfactant mixture comprises of 1.5 to 15% by weight Ethofat® 242/25; 5 to 20% by weight Glycoside® APG-325; 5 to 20% by weight Alkamuls EL-620; 2 to 15% by weight Soprophore® 3D33, and 1 to 25% by weight hexanol as a cosurfactant; the remainder being water.

25 The nature and stability of pesticidal microemulsions are influenced by the structure and chain length of the surfactant(s) and the structure of the cosurfactant. For example, solubilization increases with increase of ethoxylated alkyl phenols with same HLB. Also, solubilization increases with less
30 branching of the hydrocarbon tail. So the relative stability of the microemulsion depends on the relative packing of the

hydrophobic/hydrophilic portions of the surfactant molecule(s), which determines the binding of the interface.

5 The stable microemulsion concentrate of the present invention shows no sign of crystallization, salting-out or partition dissolution upon storing under adverse conditions ranging from -40° to 50°C, which is a considerable improvement over their EC counterparts which typically show physical instability under similar conditions. A water dilution of the concentrate generally yields solubilized particles of less than
10 about one (1) micron. This small particle size (non-gravity controlled) is advantageous in that it eliminates larger particle deposits on screens of spray application nozzles or settling out on standing due to gravity. Further, the water-based microemulsions of the present invention are more environmentally
15 acceptable than their EC counterparts which require the use of solvents.

Two ways to introduce the pesticide(s) to the other ingredients (surfactants/cosurfactants) can be employed. In the first method, the pesticides are added to and mixed with a
20 portion of the surfactants at a temperature of from about 30 - 70°. This is followed by incorporating the balance of the surfactants (some formulations contain Calcium Dodecyl Benzene Sulfonate) and the cosurfactant while maintaining the same temperature.

25 In a second method, all surfactants, cosurfactant(s) and the pesticide(s) are blended together at a temperature of from about 30 - 70°.

30 When the appropriate levels of pesticides, surfactant mixture including cosurfactant, and water are employed, it is possible to obtain clear concentrated microemulsion formulation at all levels of pesticidal concentrations. Further, upon addition

water to the concentrate at the field application rate, the dilution ranges from clear (transparent) to translucent-to-milky appearance depending on the original level of the pesticide(s) in the concentrated formulation. The lower the level of the pesticide, the clearer the diluent.

The invention will now be illustrated by the following nonlimiting examples.

FORMULATIONS EXAMPLES:

(I) PREPARATION:

a) Two-Step preparation:

Step one: The water insoluble pesticide(s) are mixed with the water-soluble surfactant, ethoxylated alkyl phenol phosphate and kept warm by a water bath maintained at 55°C.

Step two: While maintaining the 55°C temperature, a preblend of all other surfactants (ethoxylated acid, alkyl polyglycoside, ethoxylated oil and the cosurfactant, hexyl alcohol) is added to the mixture of step one, and mixing is allowed to continue for 20-30 minutes.

b) One-Step preparation:

The pesticide(s) are added to a preblend of all surfactants and cosurfactant. Allow mixing to continue for 20-30 minutes in a water bath maintained at 55°C.

(II) TYPICAL FORMULATIONS

A) 2,4-D Iso-Octyl Ester (IOE) or MCPA

A-1) Formulations composition:

5	Composition	40% wt	70% wt	90% wt	96% wt**
	2,4-D IOE	40.23	69.40	89.76	72.01
	Soprophor 3D33	6.80	3.40	0.50	1.40
	Ethofat 242/25	21.45	7.20	1.90	1.90
10	Glycoside APG-325	5.45	2.73	0.40	0.45
	Alkamuls EL-620	13.71	13.80	2.50	3.50
	Hexyl Alcohol	10.46	4.2	0.80	1.94
	Water	1.83	-----	-----	-----
	CaDDBSO3	-----	-----	4.14	4.30
15	2,4-D Acid	-----	-----	-----	14.50@@

** expressed as a total IOE;

@@ 1.00g 2,4-D Acid = 1.66g 2,4-D IOE,

14.50g 2,4-D Acid = 24.07g 2,4-D IOE and

20 Total 24.07 + 72.01 = 96.08g 2,4-D IOE.

A-2) Particle Size Analysis:

Formulation Type	Particle Size (microns)
25 40%wt ME	less than 0.1*
90%wt ME	0.4
96%wt ME	0.9
30 92%wt EC@@@	1.7

* Laser Scattering Analysis, beyond instrument detection

@@@ Commercial: Emulsifiable Concentrate, EC

B) Other Pesticide Families:

B-1) Dinitro Family : Trifluralin

B-2) Amide Family : Propanil

Formulations composition:

5

WT %	Trifluralin	Propanil
40.07	Trifluralin Tech	Propanil Tech
7.45	Hexyl Alcohol	Hexyl Alcohol
10 17.28	Ethofat 242/25	Ethofat 242/25
29.30	Alkamuls EL-620	Alkamuls EL-620
5.90	Glycoside APG-325	Glycoside APG-325

DETAILED EXAMPLES and METHOD of PREPARATION of a 100g SAMPLE

15

Example 1:

40%WT 2,4-D IOE, TWO Step Preparation

20

1. 40g of technical 2,4-D IOE was added to 6.8g Soprophor 3D33 and heated to 55°C. Label as "mix 1".
2. 13.7g Alkamuls El-620, 5.45g Glycoside APG-325, and 21.45g Ethofat 242/25 were mixed and thereafter added to a blend of 10.5g hexanol and 1.8g water. This mixture was then heated to 55° and labeled as "mix 2".
3. Mix 1 and mix 2 were then blended and mixed for 20-30 minutes at a temperature of about 55°C.

Example 2:

40%WT MCPA. TWO Step Preparation

The exact procedure of Example 1 was utilized with the exception that 40g of technical MCPA was employed as the active ingredient.

- 5 All microemulsion formulations prepared with 40% or less, including those of Examples 1 and 2 exhibit the following properties:
1. Clear amber-yellow concentrates. Upon adding water of different hardness levels (100, 342 and 1000 ppm Ca/Mg) to these microemulsions, clear transparent dilutions are generated. No settling, creaming or separation after 2 hours, 24 hours or even 6 months was observed.
 2. A particle size less than 0.1 micron.
 3. Excellent freeze/thaw storage stability over four (4) freeze-thaw cycles.
 4. Acceptable chemical stability profile, monitored and expressed as the total acid.

Example 3:

70%WT 2,4-D IOE OR MCPA. TWO Step Preparation

- 20 1. 70g of 2,4-D IOE or MCPA was added to 3.4g Soproph r 3D33 and warmed to 55°C. This was labeled as "mix 1"

2. In a second separate vessel, 13.8g Alkamuls EL-620, 2.75g Glycoside APG-325, 7.2g Ethofat 242/25 and 4.2g Hexyl alcohol were mixed and heat d to about 55°C. This was labeled as "mix 2".

- 5 3. Mix 1 and mix 2 were blended for 20-30 minutes while maintaining the temperature at about 55°C.

Example 4:

70%WT 2,4-D IOE OR MCPA, ONE Step Preparation

1. The following package of surfactants was blended:

10 3.40g Soprophor 3D33
7.20g Ethofat 242/25
2.73g Glycoside APG 325
13.80g Alkamuls EL-620 and
4.20g Hexyl alcohol.

- 15 2. About 70g of either 2,4-D IOE or MCPA technical was thereafter mixed with the surfactant package of step 1 and heated to about 55°C.

Example 5:

90%WT 2,4-D IOE, ONE Step Preparation

- 20 1. The following package of surfactants was blended:

0.50g Soprophor 3D33
1.90g Ethofat 242/25
0.40g Glycoside APG 325
2.50g Alkamuls EL-620
25 0.80g Hexyl alcohol and
4.14g Ca Dodecyl Benzen Sulphonate.

2. The above surfactant mixture was then heated to 55°C.

3. 90g 2,4-D IOE technical was then added to the heated surfactant blend and mixed for about 30 minutes while.

Example 6:

5 96%WT Expressed as 2,4-D IOE. ONE Step Preparation

1. The following package of surfactants was blended:

1.40g Soprophor 3D33
1.90g Ethofat 242/25
0.45g Glycoside APG 325
3.50g Alkamuls EL-620
1.94g Hexyl alcohol and
4.30g Ca Dodecyl Benzene Sulphonate.

and heated to about 55°C.

2. 14.5g of solid 2,4-D Acid was then added to the warm surfactant package.

3. Stirring while heating was continued until nearly all acid was solubilized.

4. 72.0g 2,4-D IOE liquid was then added to the solubilized acid/surfactant package.

5. Stirring and heating was maintained until all solid acid completely solubilized.

All microemulsion-solubilized formulations of 70% and higher including those of Examples 3-6 exhibited the following properties:

1. Clear amber liquids as concentrates. Upon adding water of different hardness to the concentrated formulations, milky dilutions are generated. No settling or separation was observed after 24 hours.

5 2. A particle size ranging from between 0.4-0.9 micron.

3. Excellent freeze/thaw storage stability; 3 cycles: from (-35°C) to room temp. to (+50°C) for 16-24 hour intervals.

4. Acceptable chemical stability, monitored and expressed as the total acid.

10 **Example 7:**

Trifluralin and Propanil, ONE Step Preparation

1. The following surfactants were blended:

17.28g Ethofat 242/25

7.45g Hexyl alcohol

15 29.30g Alkamuls EL-620 and

5.90g Glycoside APG-325.

and thereafter heated to 55°C.

2. 40g of either technical (Trifluralin or Propanil) was then added to the warm surfactant mixture.

20 3. Stirring while heating was continued until the solid technical was completely solubilized.

The microemulsion of Trifluralin does not survive freezing which is a common characteristic of formulations which incorporate the dinitro-class of pesticides.

WE CLAIM:

1. A concentrated pesticidal microemulsion which comprises from about 1% to about 99% by weight of at least one herbicidally active compound and from about 3% to about 40% by weight of a surfactant mixture, and water to 100%, wherein said surfactant mixture comprises at least one ethoxylated acid, at least one alkyl polycoside, at least one ethoxylated castor oil, optionally, at least one ethoxylated alkyl phenyl phosphate and at least one cosurfactant.
2. The microemulsion of Claim 1 which comprises from 50 to 98% pesticidal actives; from 3 to 40% surfactant mixture, and water to 100%
3. The microemulsion of Claim 1 wherein said surfactant mixture comprises 0.5 to 40% by weight of an ethoxylated acid, 0.5 to 20% by weight of an alkyl polycoside, 0.1 to 35% by weight of an ethoxylated castor oil, 0 to 15% by weight of an ethoxylated alkyl phenyl phosphate and about 0.1% to about 45% by weight of at least one cosurfactant.
4. The microemulsion of Claim 1 wherein said surfactant mixture comprises 1 to 30% by weight ethoxylated oleic acid; 1 to 15% by weight alkyl polycoside; 2 to 25% by weight of ethoxylated castor oil; 2 to 15% by weight of an ethoxylated alkyl phenyl phosphate and 1 to 25% by weight of at least one cosurfactant.
5. The microemulsion of Claim 1 wherein said at least one pesticidally active material is selected from the group consisting of 2,4-D acid, MCPA acid, straight or branched C₄-C₁₀ alkyl esters of 2,4-D acid; straight or branched C₄-C₁₀ alkyl esters of MCPA acid; bromoxynil esters of straight or branched C₄-C₁₀ alkanic acids and mixtures thereof.

6. The microemulsion of Claim 1 wherein said ethoxylated oleic acid is selected from the group consisting of Ethofat 0/15, Ethofat 242/25 and mixtures thereof; said alkyl polycoside is Glycoside APG-325; said ethoxylated castor oil is Alkamuls EL-620; said ethoxylated alkyl phenyl phosphate is Soprophore® 3D33, and said cosurfactant is hexanol.
7. The microemulsion of Claim 1 which is diluted with water to yield an aqueous-based pesticidal microemulsion which contains from about 0.05 to about 50% by weight of pesticidally active ingredients.
8. The microemulsion of Claim 1 which is diluted with water to yield an aqueous-based pesticidal microemulsion which contains from about 1.5 to about 30% by weight of pesticidally active ingredients.
9. A microemulsion surfactant package which comprises at least one ethoxylated acid, at least one alkyl polycoside, at least one ethoxylated castor oil, optionally, at least one ethoxylated alkyl phenyl phosphate and at least one cosurfactant.
10. The surfactant package of Claim 9 which comprises 0.5 to 40% by weight of at least one ethoxylated acid, 0.1 to 20% by weight of at least one alkyl polycoside, 0.1 to 45% by weight of at least one ethoxylated castor oil, 0 to 25% by weight of at least one ethoxylated alkyl phenyl phosphate and at least one cosurfactant.
11. The surfactant package of Claim 10 wherein said ethoxylated oleic acid is selected from the group consisting of Ethofat® 0/15, Ethofat® 242/25 and mixtures thereof; said alkyl polycoside is Glycoside® APG-325; said ethoxylated castor oil is Alkamuls® EL-620; said ethoxylated alkyl phenyl phosphate is Soprophore 3D33, and said cosurfactant is hexanol.

12. The concentrated pesticidal microemulsion of Claim 1 which further comprises a calcium salt of dodecylbenzene sulfonic acid

13. The microemulsion surfactant package of Claim 9 which further comprises a calcium salt of dodecylbenzene sulfonic acid

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US95/11135

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : A01N 25/30, 33/08, 37/22, 37/34, 39/04

US CL : 504/310, 317, 323, 339, 347; 71/Digest 1

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 504/310, 317, 323, 339, 347; 71/Digest 1

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
none

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

APS: microemulsi-, soprophor-, -gllcoside-, ethoxyl- phenylphosphate-, tristyrilphenyl, alkylpolygllcoside-, castor, [alkan]ols

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US, A, 5,154,754 (DAMO ET AL) 13 October 1992, column 4, lines 57-62; column 9, line 8; columns 11-12.	1-13
Y	US, A, 5,227,402 (RÖCHLING ET AL) 13 July 1993, column 1, lines 36-52; column 2, lines 1-35; column 3, lines 3-27.	1-13
Y	US, A, 4,853,026 (FRISCH ET AL) 01 August 1989, column 2, lines 1-8.	1-13
Y	US, A, 4,208,301 (GAMMON) 17 June 1980, Column 2, lines 46-58; column 3, lines 2, 65-68.	1-13
Y	US, SIR, H224 (MALIK ET AL) 03 March 1987, column 4, line 31.	1-13

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:	T	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
A document defining the general state of the art which is not considered to be of particular relevance	X	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
E earlier document published on or after the international filing date	Y	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
L document which may throw doubt on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	A*	document member of the same patent family
O document referring to an oral disclosure, use, exhibition or other means		
P document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search

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05 DEC 1995

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/US95/11135

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim
Y, P	US, A, 5,435,936 (BROZE) 25 July 1995; column 2, lines 23-47; column 3, lines 4-6; column 4, lines 33-47, columns 6-7.	1-13